Evaluating the Effects of Fertilizers on Bioavailable Metallic Pollution of soils, Case study of Sistan farms, Iran

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ABSTRACT: Present study determines not only the total amounts of metals (Cr, Cu and Pb) in superficial agricultural soil of Sistan area in Eastern Iran, but also the chemical partitioning of these elements in seven statistically selected cases. The analysis was run for local soil, soil treated by non-contaminated organic, compost and chemical fertilizers as well as soil treated by metal-contaminated fertilizers. The sampling campaign was done in Zabol University research farm in 2009. The grab samples were taken from seven different cases, the chemical partitioning analysis was performed and metallic concentrations were detected using FAAS. It may be concluded that the bioaccessibility of metals Cu and Cr would be increased in case of imposed contamination where the soil is treated with all three kinds of fertilizers. Although a relatively similar distribution pattern is seen between anthropogenic and geopogenic portions of bulk concentration in all three kinds of fertilizers, chemical fertilizer seems to manifest a more risky condition. According to the results achieved by cluster analysis, a close correlation exists between Cu and Cr behavior which may be attributed to the geological texture of the study area. In accordance with the results gained by partitioning analysis, I_{POLL} index values also show contaminated chemical fertilizer as the most risky case for all three metals in comparison with others.

Key words: Agricultural soil, Metallic pollution, Bioavailability, Fertilizer, Sistan

INTRODUCTION

Contamination caused by agricultural, municipal and industrial activities is the major cause of poor water quality among many countries (Nasrabadi *et al.,* 2010a; Nabi bidhendi *et al.,* 2007; Nasrabadi *et al.,* 2009; Karbassi *et al.,* 2007; Zhang *et al.,* 2005; Ebise and Inoue 2002; Nakano *et al.,* 2004). Poorly managed agricultural operations can lead to contamination of surface and groundwaters by nutrients and pesticides (Nasrabadi *et al.,* 2011; Novotny 1999; Gunningham and Sinclair 2005). The regular use of different types of pesticide and fertilizer products in agriculture will cause dispersion within the environment by means of drift, run-off and drainage (Kolpin *et al.,* 1998; Guzzella et al. 2006). This may result in residues being encountered in groundwaters (Lacorte and Barcelo 1996), river waters (Irace-Guigand *et al.,* 2004; Claver *et al.,* 2006), and also in coastal waters and lakes (Konstantinou *et al.,* 2006), suggesting that mobilization can occur and that residues can be found far away from the point of application.

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Lots of studies on runoffs from agricultural zones have been carried out detecting various fertilizers and pesticides in different hydrological and soil conditions (Karpouzas *et al.,* 2005; Miao *et al.,* 2003; Nakano et al. 2004; Villa *et al.,* 2003). In Iran, agricultural activities are highly dependent on the use of fertilizers and pesticides due to climatic and soil conditions, thus posing a potential risk to the quality standards of water resources.

Composting is defined as the biological decomposition and stabilization of organic substrates under conditions which allow development of thermophilic temperatures as a result of biologically produced heat, with final products sufficiently stable for storage and application to land without adverse environmental effects (Polprasert, 1996). In general, the chemical and physical characteristics of compost would vary according to the nature of the starting material, the condition under which the composting operation is carried out and the extent of the decomposition (Hamuda *et al.,* 1998).

Amendment with compost alone may initially increase plant growth by improving the nutrient status of the soil and by immobilisation of metals, but after degradation of the organic matter of the compost, the adsorbed metals might be released and become available again to plants and animals. In contrast to the wide publication of many studies which report the immobilisation of metals with composts, a limited number report the possibility that compost amendments increase the leaching or extractability of metals. For example it has been shown that certain composts in combination with specific soils increase arsenic leaching (Cao *et al.,* 2003; Mench *et al.,* 2003). There are also references on the mobilization effects of composts on other metals of concern. Clemente et al. (2006) reported increased bioavailability of copper after amendment of a soil from a lead-zinc mine area with a compost made from olive leaves and the solid fraction of olive-mill waste water. Interestingly, both zinc and lead were effectively immobilised by the compost. Dissolved organic matter is known to mobilise Cu and Pb through complexation but not Cd and Zn (Bradl, 2004).

Due to the toxicity and ability of the heavy metals to accumulate in the biota, pollution by these metals is a serious problem (Morillo *et al.,* 2002). One of the most crucial properties of these metals, which differentiate them from other toxic pollutants, is that they are not biodegradable in the environment (Rauret *et al.,* 1999). The heavy metal concentration in aquatic ecosystems has increased considerably as a result of inputs from human production and consumption activities (Nabi Bidhendi *et al.,* 2007).

Information on total concentrations of metals alone is not sufficient to assess the environmental impact of polluted sediments because heavy metals are present in different chemical forms in sediments (easily exchangeable ions, metal carbonates, oxides, sulfides, organometallic compounds, ions in crystal lattices of minerals, etc.), which determine their mobilization capacity and bioavailability (Yu *et al.,* 2001). Several methods for determining the different forms of metals in sediments are described in the scientific literature (Nasrabadi *et al.,* 2010b). The most widely used methods are based on sequential extraction procedures whereby several reagents are used consecutively to extract operationally defined phases from the sediment in a sequence. For this study, the sequential extraction procedure proposed by the European Union's Standards, Measurements, and Testing program was taken in to consideration (Rauret *et al.,* 1999; Morillo *et al.,* 2002; Nasrabadi *et al.,* 2020b). This scheme consists of three successive extractions that allow us to associate the metals with one of the following

phases: acid-soluble phase (fraction 1), reducible phase (fraction 2), oxidizable phase (fraction 3), and a fourth phase—residual or inert (fraction 4).

Present study determines not only the total amounts of metals (Cr, Cu and Pb) in superficial agricultural soil of Sistan area in Eastern Iran, but also the chemical partitioning of these elements in seven statistically selected cases. The analysis was run for local soil, soil treated by non-contaminated organic, compost and chemical fertilizers as well as soil treated by metal-contaminated fertilizers. Such finding makes it possible to know the mobility of metals in the soil and accordingly their bioavailability in the environment. Furthermore, a couple of soil metallic pollution indices are also considered to evaluate the degree of pollution within the study area.

MATERIALS & METHODS

The sampling campaign was done in Zabol University research farm in 2009. The study area is located in 61° 31" longitude and 31° 2" Latitude with an approximate altitude of 478 meters from sea level. The field was divided into squares with one square meter of surface area. In non-contaminated segments the soil was simply treated by organic, compost and chemical fertilizers while in the metal-contaminated segments the treated soil was also exposed to $CuCl_2.2H_2O$, $CrCl_3.6H_2O$ and $Pb(No_3)_2$ to simulate the metallic pollution. The Grab samples were taken from seven different cases. The samples were immediately sealed and stored at 4_C until their arrival at the laboratory. Grain size fraction less than 63 *l*m was chosen for analysis (Nasrabadi *et al.,* 2010a; Karbassi *et al.,* 2007). All the sieving and sequential extraction procedures were performed in a glove box purged with nitrogen (Lopez-Sanchez *et al.,* 1996). The total metal content was determined by digesting the samples with a mixture of HNO3–HClO4 in a microwave oven. CEM 3010 high-pressure digestion bombs (consisting of a body made of a specific microwave-transparent polymer with a Teflon cup and cover) were used for sample digestion. These bombs, designed specifically for microwave heating, are chemically inert and combine the advantages of closed highpressure (13.8 bar) and high-temperature digestion. The concentration of the analytes in this solution was analysed by FAAS (Khajeh,,2009).The chemical partitioning of metals was determined by means of the sequential extraction scheme proposed by the European Union's Standards, Measurements and Testing Program (SM and T, formerly BCR). This scheme consists of three successive extractions (Table 1) that make it possible to determine the association of the metals in three phases: acid-soluble, reducible and oxidizable.

Table 1. Extractants used in each extraction step and the extraction phases of sediments in the sequential extraction procedure (Morillo *et al.,* 2002)

Extraction step	Reagent—concentration—time	Sediment phase
1	Acetic acid (CH3COOH)—0.11 mol l _ 1—16 h	Acid-soluble (exchangeable ions, carbonates)
2	Hydroxylamine hydrochloride (NH$_2$OHHCl)—0.5 mol l _ 1 (pH 2 with HNO$_3$)—16 h	Reducible (iron/manganese oxides)
3	Hydrogen peroxide H$_2$O$_2$—8.8 mol l _ 1—1 h at room temperature + 2 h at 85 °C+ ammonium acetate (CH3COO NH$_4$)—1.0 mol l _ 1 (pH 2 with HNO$_3$)—16 h	Oxidizable (organic substances and sulfides)

Furthermore, a fourth phase, residual or inert (fraction 4), was determined as the difference between the total metal content and the sum of the contents in the three previous phases.

RESULTS & DISCUSSION

Bulk and chemical partitioning concentrations of metals Cu, Pb and Cr in local soil are shown in Table 2. In comparison with average shale values, the bulk concentration of Cu and especially Cr are far below the common limits. However, the Pb bulk concentration is roughly twice as the one in shale.

Bulk and chemical partitioning concentrations of metals in the soil samples treated by clean (Table 3) and metal-contaminated fertilizers (Table 4) are also analyzed. Three different kind of fertilizers (organic, compost and chemical) are considered in each analysis campaign.

To assess the intensity of metal contamination in soil samples, the geochemical accumulation index was calculated using:

$$I_{geo} = Log_2 [C_n/(1.5 \times B_n)] \qquad (1)$$

Where I_{geo} is the geochemical accumulation index, C_n is the sediment metal concentration and B_n is the metal concentration in the shale (Gonzalez-Macias *et al.,* 2006; Forstner et al. 1990; Muller 1979).

In the present study, a newly developed formula which is a modification of the I_{geo} is introduced as follows ((Karbassi *et al.,* 2008):

$$I_{POLL} = Log_2 [B_c/L_p] \qquad (2)$$

Table 2. Chemical partitioning of metals in local soil (mg/kg)

Metal	Bulk Concentration	Exchangeable Concentration	Reducible Concentration	Oxidizable Concentration	Anthropogenic %	Geopogenic %	Shale values
Cu	22.94	5.33	.75	1.17	31.6	67.4	45
Pb	38.36	17.84	6.3	2.28	68.8	31.2	20
Cr	3.79	.65	.21	.32	31.1	68.9	90

Table 3. Chemical partitioning of metals in soil treated by non-contaminated fertilizers

Metal	Bulk Concentration	Exchangeable Concentration	Reducible Concentration	Oxidizable Concentration	Anthropogenic %	Geopogenic %
Organic Fertilizer						
Cu	24.1	5.856	.752	1.386	33.2	66.8
Pb	41.81	21.11	6.52	2.65	72.4	27.6
Cr	4.31	.774	.232	.407	32.8	67.2
Compost						
Cu	25.67	5.69	.64	1.62	31	69
Pb	43.56	21.18	5.62	2.97	68.4	31.6
Cr	4.53	.84	.15	.46	32.2	67.8
Chemical fertilizer						
Cu	23.21	5.9	.84	1.13	33.9	66.1
Pb	39.12	18.75	6.37	2.26	70	30
Cr	3.86	.703	.16	.346	32.6	67.4

Table 4. Chemical partitioning of metals in soil treated by metal-contaminated fertilizers

Metal	Bulk Concentration	Exchangeable Concentration	Reducible Concentration	Oxidizable Concentration	Anthropogenic %	Geopogenic %
Organic fertilizer						
Cu	52.96	31.85	.97	.78	63.5	36.5
Pb	115	60.53	1.06	6	58.8	41.2
Cr	17.44	9.36	.85	1.60	67.8	32.2
Compost						
Cu	65.26	28.1	.646	1.88	46.9	53.1
Pb	123.25	60.83	1.04	6.62	55.6	44.4
Cr	19.3	10.97	.52	2.32	71.6	28.4
Chemical fertilizer						
Cu	40.7	29.4	.376	.746	75	25
Pb	106.7	56.86	2.16	7.02	62	38
Cr	14.24	9.3	.46	.675	73.3	26.7

Table 5. I$_{geo}$ values for the soil treated by contaminated and non-contaminated fertilizers

Metal	Local soil	Non-contaminated organic fertilizer	Non-contaminated compost	Non-contaminated chemical fertilizer	contaminated organic fertilizer	contaminated organic fertilizer	contaminated organic fertilizer
Cu	-1.35	-1.27	-1.18	-1.34	-0.14	0.15	-0.52
Pb	0.15	0.27	0.33	0.18	1.73	1.83	1.62
Cr	-3.94	-3.76	-3.69	-3.92	-1.74	-1.60	-2.03

Table 6. I$_{poll}$ values for the soil treated by contaminated and non-contaminated fertilizers

Metal	Local soil	Non-contaminated organic fertilizer	Non-contaminated compost	Non-contaminated chemical fertilizer	contaminated organic fertilizer	contaminated compostfertilizer	contaminated chemicalfertilizer
Cu	0.56	0.58	0.53	0.59	1.45	0.91	2.00
Pb	1.68	1.85	1.66	1.73	1.27	1.17	1.39
Cr	0.53	0.57	0.56	0.56	1.63	1.81	1.90

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Dendrogram using Average Linkage (Between Groups)

        Rescaled Distance Cluster Combine

 C A S E      0         5        10        15        20        25
Label    Num  +---------+---------+---------+---------+---------+

 Cu        1   ─┐
               │└────────────────────────────────────────────────┐
 Cr        3   ─┘                                                 │
                                                                  │
 Pb        2   ───────────────────────────────────────────────────┘
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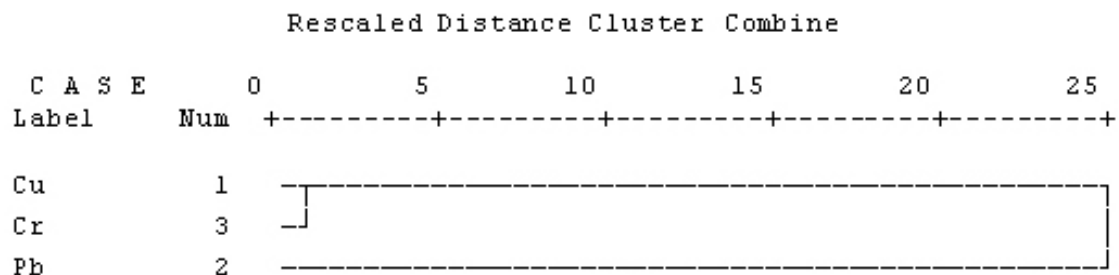
Fig. 1. Dendrogram showing clustering of metals

Where I_{POLL}, B_c, and L_p are indicative of pollution intensity, bulk concentration, and lithogenous portion, respectively. Muller as well as other researchers, have used the concentration of metals in shale as a substitute for B_n, and applied a factor of 1.5 for normalization to background metals concentrations. In the present study, B_n was computed by subtraction of the anthropogenic portion of metals from bulk concentration. Since there was not any need in these evaluations to use the shale metal concentrations, the constant factor (1.5) was eliminated. A comparison among various pollution indices in soil samples is shown in Tables 5 and 6.

In order to assess the initiation and also the behavior similarity of studied metals the cluster analysis using Euclidean distance as linkage method was taken into consideration. The results of the cluster analysis are presented in the form of a dendrogram (Fig. 1), which shows the degree of similarity among the behavior of metals in different samples.

CONCLUSION

The current study determines the bulk concentration and also the chemical partitioning of metals (Cr, Cu and Pb) in superficial agricultural soil of Sistan area in Eastern Iran in samples collected from local soil, soil treated by non-contaminated organic, compost and chemical fertilizers as well as soil treated by metal-contaminated fertilizers. It is concluded that a similar pattern exists in metallic bulk concentrations as well as partitioning phases (exchangeable, reducible and oxidizable concentrations) between the virgin soil and the one treated by clean fertilizers (Tables 2 and 3). In other words, non of the fertilizers may remarkably change the soil affinity of sorption/desorption processes in case where no metallic pollution is imposed. However, another scenario is observed when the soil is exposed to metallic pollution (Table 4). The anthropogenic portion of metals Cu and Cr is approximately doubled in soil samples treated by contaminated fertilizers in comparison with virgin soil samples. Conversely, the mobility of Pb is slightly decreased in the latter case. Accordingly, it may be concluded that the bioaccessibility of metals Cu and Cr would be increased in case of imposed contamination where the soil is treated with all three kinds of fertilizers. Although a relatively similar distribution pattern is seen between anthropogenic and geopogenic portions of bulk concentration in all three kinds of fertilizers, chemical fertilizer seems to manifest a more risky condition. Such slight difference may be due to the lack of organic materials in chemical fertilizers in comparison with compost and organic ones which decrease the formation of organo-metallic compounds. According to the results achieved by cluster analysis,

a close correlation exists between Cu and Cr behavior which may be attributed to the geological texture of the study area. Regarding Pb, the high bulk concentration (around twice the average shale value), the remarkable anthropogenic share in total concentration (around 70 %) as well as the behavior independency to other two metals indicate a relatively different source. Proximity of studied farms to the main road and consequently being exposed to a gradual long-term load of vehicle fuels in different forms may be introduced as the main reason of such metallic pollution in the samples. Regarding index approach, as the geochemical index does not consider the bioavailable metallic pollution of soil samples and just focuses on the comparison between the existent bulk concentrations with that of shale, the interpretation of index values falls mostly within the not polluted category. However, as it was indicated before the Pb status is changed between not polluted and slightly polluted level because of its high initial concentration. On the other hand, I_{POLL} smoothly intervenes the role of bioavailable contamination in final interpretation. Accordingly the pollution level of Cu and Cr in contaminated fertilizers is reported to be slightly polluted while the one in clean fertilizers is not polluted. Furthermore, in accordance with the results gained by partitioning analysis, I_{POLL} values also introduce contaminated chemical fertilizer as the most risky case for all three metals in comparison with others.

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